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THIOUREA LEACHING OF SILVER-BEARING MATERIALS I. LITERATURE SURVEY

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THIOUREA LEACHING OF SILVER-BEARING MATERIALS

I. LITERATURE SURVEY

by

R.M. Morrison*

ABSTRACT

The available literature on the use of thiourea for leaching silver materials is surveyed. The reasons for considering thiourea, the general chemistry of thiourea, gold and silver thiourea chemistry, and the use of thiourea in the extractive metallurgy of gold and silver are discussed. It is concluded that much more fundamental and applied work is needed before rational decisions on the effectiveness of thiourea for silver leaching can be made. Some suggestions for introductory studies on the application of thiourea to silver extraction are outlined.

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LA LIXIVIATION PAR LA THIOUREE DE MATERIAUX

CONTENANT DE L'ARGENT

I. ENQUETE SUR LA DOCUMENTATION

par

R.M. Morrison*

RESUME

On a mené une enquête sur la documentation existant quant au procédé de lixiviation au moyen de la thiourée pour les matériaux contenant de l'argent. Le présent rapport discute des raisons pour prendre en considération ce procédé, ainsi que de la chimie générale de la thiourée, des réactions chimiques de la thiourée avec l'or et l'argent, et de l'utilisation de la thiourée pour la métallurgie extractive de l'or et de l'argent. On a conclu qu'il fallait encore beaucoup de travaux fondamentaux et appliqués avant de pouvoir prendre une décision rationnelle quant à l'efficacité de la thiourée pour la lixiviation de l'argent. On présente également quelques suggestions pour des études fondamentales sur l'application de la thiourée à l'extraction de l'argent.

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INTRODUCTION

Cyanidation, a commercially and technologically successful process, has been the principal method of extracting gold and silver from their ores. The main drawbacks to the process are excessive cyanide consumption by certain elements, relatively slow dissolution rates of gold and silver minerals, and its inability to attack and solubilize some refractory materials. Other extractive systems have been considered to supplement cyanidation in order to overcome these problems.

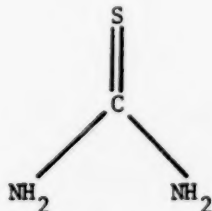
Thiourea has been utilized as a leaching agent for gold and silver. For instance, it has been shown that gold metal can be dissolved much more quickly by thiourea than by cyanidation (1). According to Groenewald (1), gold dissolution with thiourea was first reported by Russian workers in 1941. From the 1960's onward, there has been much work done on various aspects of thiourea in hydrometallurgical and inorganic chemistry. Groenewald has reviewed the chemistry of gold and thiourea to 1976 (1); this reference is useful because it covers much of the work done by the early Russian workers.

It should be emphasized that thiourea of ores is not yet in commercial operation in North America. There have been reports of a pilot plant module being offered for sale (2) that is based on this process. Also, a recent conference sponsored by AIME on the economic recovery of gold and silver included a paper on thiourea leaching of gold and silver (3). Outside North America, there is some indication of commercial thiourea. At Vieille-Montagne, Viviez, France, there is an operating thiourea plant treating silver residues from an electrolytic zinc operation. The Russian literature has many references to thiourea chemistry and hydrometallurgy perhaps suggestive of some application there. Unfortunately, very little information is available from these sources.

There is an interest in evaluating the thiourea leaching of silver materials for CANMET's Silver Recovery in the Zinc Industry Project. Thiourea, being an organic moiety, presents some unique chemical features which are not seen in other processing systems. This review will examine some of the chemistry of thiourea and its relation to silver leaching. Although the primary concern is with thiourea leaching of silver, silver minerals, and silver-bearing materials, most work on thiourea has been reported on gold. That work will also be discussed briefly since much of the chemistry of thiourea has been derived from those studies. Finally, the chemistry of thiourea with silver and the use of thiourea in the extractive metallurgy of silver will be covered. The aim of this review is to collate the knowledge gained from previous research and to assess what is known about these systems. Decisions regarding the application of these methods for leaching silver-bearing materials is the intended ultimate result of this investigation.

GENERAL CHEMISTRY OF THIOUREA

Thiourea, as the name indicates, is the sulphur analogue of urea; rarely, thiourea is also called thiocarbamide. The formula of thiourea is $\text{H}_2\text{N}(\text{C}:\text{S})\text{NH}_2$ and it has the structure:

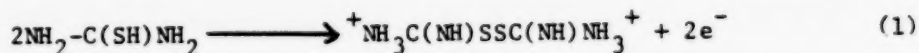


The thiol function of the molecule is the C=S group. Thiourea also interconverts with isothiurea ($\text{H}_2\text{N}(\text{C}-\text{SH})\text{NH}_2$), a mercaptan, via tautomerism (4). The abbreviation for thiourea is generally "tu".

Thiourea is fairly stable in neutral solution but decomposes rapidly in basic solutions. In acidic solutions, the decomposition is slower and has been reported (5) to proceed from the protonated thiourea to H_2S and cyanamide (NH_2CN) which in turn hydrolyses to urea ($(\text{NH}_2)_2\text{CO}$).

Thiourea in aqueous solutions is not a Bronsted acid or base. The pK_a of the conjugate acid of thiourea is -1.19 (6) and thiourea will not protonate except in the most acidic media. The apparent acidity constant (pH^*) of thiourea in water is 14 (7). The thiol functionality, however, is a good Lewis base and will bind Lewis acids such as transition metals. Thiourea is a sulphur donor ligand and readily forms complexes with first row transition elements. For example, the fluoride, chloride, iodide, perchlorate, nitrate, thiocyanate, tetrafluoroborate, and sulphate compounds of nickel thiourea are known (8). Thiourea can be classed as a soft or class b donor ligand according to Pearson's HSAB (9) theory. Thiourea has a great tendency to react with soft acids such as the second and third row transition elements; this fact may account for the propensity of gold and silver-thiourea complex formation.

Thiourea also possesses some redox chemistry. When reacted with oxygen or hydrogen peroxide, thiourea will form formamidine disulphide (10). The half-cell reaction of the thiourea/formamidine disulphide couple is:



This reaction is reversible on platinum and has a standard reduction potential of 0.420 volts (10). The reduction potential is independent of hydrogen ion concentrations at $\text{pH} = 0.4\text{-}3$. The formamidine disulphide is the oxidizing agent when oxygenated thiourea solutions are used as a leaching medium. Thus, thiourea can serve double duty as an oxidizing agent (via formamidine disulphide formation) and as a complexing ligand to solubilize the metal.

Thiourea and ferric ion form a complex identified as $[\text{FeSC}(\text{NH}_2)_2]^+$ which has a stability constant of 6.64 (1) and tends to stabilize the thiourea in that form. Although the potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple is high enough to cause formamidine disulphide production, the reaction occurs slowly. As a result, thiourea is considered to be more stable in ferric ion media than in the presence of other oxidizing agents in acidic solution. This iron(III) complex has shown some interesting chemistry. It has been used in polymerization reactions which require free radicals as the initiator (11,12); this property has been attributed to the mercaptan functionality available through "tauterism". Also, the decomposition of this thiourea complex is catalysed by the presence of copper or gold. This fact has been the basis of a kinetic determination for these elements (13). Here, the rate of disappearance of the 520 nm absorbance line of $\text{Fe}(\text{tu})^{3+}$ is proportional to the amount of copper or gold in solution.

Thiourea, being a polar molecule, is soluble in aqueous solution. In pure water, the solubility is estimated at 120 g L^{-1} at 20°C (14,15). Thiourea is more soluble in strongly acidic media and displays some interesting chemistry with hydrochloric acid showing the most complicated behaviour. In hydrochloric acid at 20°C , the solubility of thiourea increases greatly with added HCl (0-10%), until a maximum solubility is reached (400 g L^{-1}). With more added HCl, the solubility of thiourea decreases until a minimum solubility (300 g L^{-1}) is observed around 15% HCl. For HCl concentrations greater than 15%, further addition of acid increases the solubility to a maximum (320 g L^{-1}) at $\sim 19\%$ HCl. Additions of $>19\%$ HCl cause the solubility of thiourea to diminish quite rapidly. This behaviour has been attributed to different crystallization species; in the initial rapidly ascending solubility regime, tu is the solid species; after the first maximum,

$(tu)_2 \cdot HCl$ is the solid and after the second maximum, $tu \cdot HCl$ is the solid phase. In strong acids such as $HClO_4$ and HI , the solubility of thiourea increases with added acid till approximately 40% acid is present; the maximum solubilities are $\sim 500 \text{ g L}^{-1}$ ($HClO_4$) and 450 g L^{-1} (HI). Above these acid concentrations the solubility of thiourea decreases rapidly. Similar behaviour has been observed for nitric acid where a tu maximum has been observed at 10-15% HNO_3 . The involvement of $tu \cdot HA$ in these three systems has been postulated. With oxalic acid, phosphoric acid (H_3PO_4), and boric acid, the addition of acid does not have as large an effect on the solubility. It should be noted that boric acid (H_3BO_3) additions actually decrease the solubility of thiourea.

The analysis of solutions for thiourea can be done by a variety of different methods. Oxidimetric, complexation, desulphurization, acidimetric, colorimetric and miscellaneous methods of analysis have been reviewed by Gupta (16). One of the more popular methods is complexation with mercuric salts (17) followed by potentiometry. Also, thiourea is polarographically active with a half-wave potential of +0.02 volts vs SCE in 0.05 H_2SO_4 electrolyte due to the formation of $Hg(tu)_{2-4}^+$ (18). All these methods can be subject to interferences from other elements and each analytical situation should be examined individually.

The environmental chemistry of thiourea is also of some concern (19). A lethal dose of thiourea for human beings is 10 grams per kilogram of body mass. Apparently, the compound is carcinogenic to rats and trout but has not been shown to be a carcinogen to human beings. When compared to cyanide, an acutely poisonous substance both in its own right and because of HCN formation at $pH < 9$, thiourea is fairly innocuous. The effects of the discharge of organic and high acid concentrations in the effluent stream would have to

be considered. Any large scale operations using thiourea would require a more careful evaluation of the impact of thiourea in the work place and on the environment.

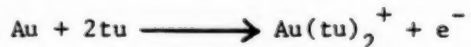
Thiourea is presently used in the metallurgical industry as a levelling agent in electrolytic processing. For instance, thiourea is added in trace amounts to copper sulphate electrowinning electrolytes to produce compact, coherent deposits (20). Thiourea, being a polar molecule, can adsorb on metal surfaces and this property is utilized in the electrochemical industry.

THIOUREA AND GOLD

Before reporting the use of thiourea in the extractive metallurgy of gold, the nature of the interaction of thiourea with gold will be discussed. Information on the type of complex ions formed, the extractability of the complexes, the stability of complexes, and the electrochemistry of gold will be examined briefly.

Gold(I) forms a bithiourea complex, $\text{Au}(\text{tu})_2^+$. The complex $[\text{Au}(\text{tu})_2\text{NO}_3]$ has been made (21) and $(\text{Au}(\text{tu})_2)[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$ has been isolated from the organic phase after the extraction of thiourea-gold solutions into nitrobenzene in the presence of $\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2^-$ (22). Gold(III) oxidizes thiourea.

Gold metal will dissolve in thiourea solutions according to (23):



The reduction potential of the reaction is 0.352 V on a fresh surface and 0.41 volts on a passivated surface (24). The corresponding E values for gold dissolution in non-complexing (i.e., SO_4^{2-} , ClO_4^-), chloride, bromide, thiocyanate and cyanide media are 1.82, 1.11, 0.06, 0.69 and -0.60 volts,

respectively. This information means that in thiourea solution, gold is less noble than all solutions other than cyanide. Clearly gold is more easily oxidized in thiourea solution than in the other systems which are alternatives to cyanide.

Because of this reduced nobility of gold in thiourea solutions, some oxidizing agents normally too mild for gold leaching can be employed. For example, ferric ion ($E = 0.71$ volts) possess enough oxidizing power to be used. The thiourea-formamidine disulphide couple (0.42) also may be used. Oxidants such as these possess some advantages over the conventional cyanide-oxygen system; i.e., molecular oxygen dissolved in solution. Whereas the concentration of dissolved oxygen at ambient temperatures and 1 atm pressure is 8 mg L^{-1} , the concentrations of ferric ion can be as high as 2 molar and thiourea as high as 1 molar. Thus, the overall rate of reaction can be increased by increased reagent (oxidant) concentration even though the rate constants may be similar. With the thiourea couple, it may be that oxygen is the active oxidant and thiourea is just a catalyst; this would increase the reaction rate as is desired.

THIOUREA IN THE EXTRACTIVE METALLURGY OF GOLD

A few reports on the use of thiourea as a leaching agent for gold-bearing materials have been published in the last ten years. Groenewald has studied some variables affecting the dissolution of a gold rotating disk and a ground gold ore (23). Chen et al. have studied thioureaation of a gold rotating disk and of a copper concentrate containing gold (25). Pyper and Hendrix have reported on the thioureaation of Chipmunk ore (19). It is useful to survey these reports to ascertain the range of concentrations of reagents used and their effects on the rate and extent of reaction.

The first Russian workers on thiourea leaching of gold (26) reported that they used temperatures of 15° to 40°C, 0.1-9% thiourea concentration in 0.1-0.5% H_2SO_4 with oxidant levels of H_2O_2 (0.03-0.06%), Na_2O_2 (0.1%), FeCl_3 (0.5%), or $\text{Fe}_2(\text{SO}_4)_2$ (4%) to effect the dissolution of metallic gold. They found that 89% of the Au was extracted from a Cu-containing ore with 2% tu, 0.5% H_2SO_4 and 0.5% FeCl_3 after preliminary leaching of the ore with 1-5% H_2SO_4 . They also reported 96% extraction of Au from a Sb-containing concentrate, 8% more than cyanidation could accomplish. The reagents used by subsequent workers tend to be in the range reported by the earlier Russian workers.

Groenewald (23) used a rotating Au disk and thiourea solutions (tu 0.001-0.1 M; H_2SO_4 0.01-0.1 M; $\text{Fe}_2(\text{SO}_4)_2$ 0.001-0.01 M; formamidine disulphide (FDS) 0.001-0.01 M) to examine the dissolution of gold. In 0.1 M H_2SO_4 , 0.1 M tu and variable Fe^{3+} (0.001-0.01 M), the rate of Au dissolution increased with ferric ion concentration but the activity of the solution decreased more quickly with time because of the decomposition of thiourea by ferric ion. In another experiment, it was found that in 0.01-0.05 M H_2SO_4 , there was no rate dependence on the rotation speed (ω) when the tu: Fe^{3+} ratio was less than or equal to unity. There was a $\omega^{1/2}$ dependence of the rate when this ratio was 10. This was interpreted to mean that sufficient thiourea must be present to complex the gold, otherwise the reaction is not diffusion controlled; i.e., thiourea must be present in large excess for the reaction to be fast.

Groenewald also used FDS as an oxidant. It was generated in situ by addition of peroxide to thiourea with FDS being monitored potentiometrically; as was discussed previously the tu/FDS couple is reversible and gives a

linear response to $\log(tu^2:FDS)$. Using 0.1 M H_2SO_4 - 0.1 M tu and variable FDS (0.001-0.01 M), the rate of gold dissolution increased with increasing FDS concentration. At 0.1 M H_2SO_4 and 0.1 M FDS with variable tu (0.001 M-0.1 M) concentration, the rate increased with increasing thiourea concentration. The temperature dependence of the gold dissolution rate in 0.1 M H_2SO_4 , 0.1 M tu and 0.01 M FDS gave an activation energy of 28 kJ/mole indicative of diffusion control. It was found that there was rapid decomposition of thiourea at temperatures $\geq 45^\circ C$. Additional experiments using bubbled air or oxygen to oxidize thiourea to FDS showed that the oxidation rate was only 15% of that found using the peroxide.

Chen et al. used similar conditions in their studies on the rotating gold disk (25). In 1% (0.13 M) thiourea and 0.5% (0.05 M) H_2SO_4 , the reaction rate was dependent upon the ferric ion concentration in 0.04-0.24% (0.007-0.040 M) Fe(III) solution. A linear relationship between the dissolution rate and $w^{\frac{1}{2}}$ for $w \leq 327$ RPM was observed, consistent with a diffusion controlled reaction. At rotation speeds greater than 327 RPM, the rate did not change greatly. Although the authors claim that above 327 RPM non-laminar flow is observed, this seems highly unlikely. These workers also compared the relative rates of cyanidation and acidothioureation. With 0.5% NaCN and 0.05% CaO, they found a gold dissolution rate of $3.54 \times 10^{-4} \text{ mg cm}^{-2} \text{ s}^{-1}$; with 1% thiourea, 0.5% H_2SO_4 and 0.1% (0.018 M) Fe(III), they found that the rate was 12.2 times faster than with cyanide.

Groenewald (23) also studied the thioureation of a ground gold ore. The ore assayed 15 grams Au per ton and contained particles which were 65% $< 75 \mu\text{m}$. Most of the work was done on an acid-treated fraction. When

the ore was not acid leached beforehand, there was more acid soluble iron present that tended to lower the Au extraction.

With the acid-treated ore, the use of 0.01 M, 0.03 M and 0.1 M thiourea in 0.5 M H_2SO_4 with air agitation gave 20, 50 and 90% extractions, respectively, after 6 hours. Under stronger leaching conditions (1.0 M H_2SO_4 , 1.2 M thiourea and 0.1 M H_2O_2) 99% of the gold was dissolved in 1 h, a very fast rate. Solutions containing 0.05 M H_2SO_4 , 0.12 M thiourea and 0.01 M H_2O_2 were found to give greater rates of dissolution and lower residual Au assays than conventional cyanidation media (0.025% KCN, 0.25% CaO and $0.004 \text{ gL}^{-1} \text{ Pb}(\text{NO}_3)_2$).

Although good rates of reaction and efficient extractions of Au were obtained, the consumption of thiourea was a problem. Groenewald quoted the following values: for 0.1 M thiourea solution, 0.4 kg thiourea was consumed per ton of ore, and for 1.0 M thiourea, 1.4 kg per ton of ore. The cost of tonnage thiourea is approximately \$2/kg. The presence of iron(III) in the slurries was identified as a major source of thiourea consumption. Much of the formation of colloidal sulphur, indicative of thiourea decomposition, occurred prior to leaching during the preparative stage and the effect was noted to be worse in more concentrated thiourea solutions. Temperature also is a factor as shown by the rotating disk work; increasing temperatures also favour thiourea decomposition.

Groenewald's conclusion on the use of thiourea as a leaching agent is that the consumption of thiourea makes the process uneconomical. If an extremely high rate of gold extraction is needed; e.g., for assaying, etc., thiourea could be very useful. It should be noted that Groenewald elsewhere writes of applications of thiourea in other areas such as electrodeposition and recovery of gold (1).

Chen et al. used thiourea to leach an acid-washed copper concentrate (25). They found that (0.5% tu, 0.5% H_2SO_4 , 0.1% Fe(III)) acidthioureaation gave slightly higher rates and slightly better extractions than cyanide (0.5% NaCN, 0.5% CaO) solutions. They claimed that the thiourea solution, unlike cyanide, did not solubilize the copper. These workers did not mention any problems with excessive thiourea consumption. They used relatively favourable conditions such as low concentrations of thiourea, ferric ion, and acid, and the work was done at room temperature ($\sim 20^\circ C$).

Pyper and Hendrix have reported on their laboratory scale thioureaation studies on Carlin-type ore from the Chipmunk property in Nevada (19). Carlin-type deposits are characterized as micron-sized, high fineness gold particles in a dolomitic sandstone. In the Chipmunk ore, the gold is in a quartz matrix with minor amounts of dolomite and muscovite, and assays 2.4 grams Au per ton of ore. Carbonaceous material is present, but is not activated and does not interfere with the extraction of Au by cyanide or thiourea.

The extraction of gold was studied over the range of pH 0-6, thiourea levels of 10 kg to 200 kg per ton of ore, in the absence and presence of ferric sulphate levels of 0 to 100 kg per ton, and as a function of temperature ($10-60^\circ C$). Generally it was found that better extractions were obtained with decreasing pH, medium thiourea concentrations (35 kg/ton), at lower ferric ion concentrations (5 kg/ton) and at lower temperatures ($20^\circ C$). Under these favourable conditions, gold extractions were 80-90% after 8 to 10 hours of leaching. Higher thiourea loadings gave faster extractions, but excessive thiourea consumption resulted.

Thiourea consumption is a major factor in process viability, and was studied extensively by Pyper and Hendrix. They found that at lower

thiourea loadings (35-40 kg/t), the rate of thiourea consumption increased with leaching time for the first twenty hours and decreased thereafter. Higher thiourea levels gave greater levels of consumption as did increased ferric sulphate concentrations and temperatures higher or lower than 20°C. An inverse relationship was observed between the % extraction-time and thiourea consumption-time curves. The thiourea solutions which gave the best extractions of gold had the most "free" thiourea present. The consumption of thiourea was typically 10 kg per ton and could rise to 20 kg per ton at higher thiourea loadings, higher ferric sulphate concentrations and higher temperatures. These consumption or decomposition levels are well above those reported by Groenewald in his ore leaching work (23).

Pyper and Hendrix also studied the effect of the oxidation potential. It was found that a potential of at least +150 mV was necessary for 80-85% extraction but that higher potentials did not significantly increase the amount of gold dissolved.

The authors concluded that commercial thioureation of Chipmunk ore is feasible but due to high thiourea and sulphuric acid consumption, is uneconomic. Cyanidation of the Chipmunk ore is quicker and gives similar extractions to the thioureation and does not present reagent consumption problems. Thus, thioureation does not possess any special advantages for this type of ore.

One of the most common methods of precipitating gold from cyanide solution is cementation on zinc dust. This method would not be appropriate for acid solutions encountered in thioureation and alternate methods would have to be employed. Carbon in pulp, ion exchange, and electrolysis, which are also used in cyanidation may be adapted for thiourea solutions (27,28). Cementation with other metals such as lead, is also an alternative (29).

THIOUREA AND SILVER

One of the major purposes of this survey is to ascertain the effectiveness or potential effectiveness of thiourea as a lixiviant for silver-bearing materials. The general chemistry of thiourea and the practical work done on the extractive metallurgy of gold have provided a basis for evaluating the use of thiourea for silver. Before considering the extractive metallurgy of silver with thiourea, the chemistry of silver in thiourea solutions will be examined.

To understand the interaction of silver and thiourea, some data on compound formation between them must be obtained. Since silver (+1) is a d^{10} metal ion, it is unlikely that spectroscopic or magnetic measurements will be useful for determining the stereochemistry of Ag complexes. More indirect methods such as potentiometry, solubility measurements and solid-state compound structure will have to be used to elucidate the nature of thiourea and silver solution chemistry. The most readily obtainable information will be the stoichiometry of the solid compounds, stability constants of complex formation, and stability of the compounds in various media.

Thiourea has been shown to solubilize silver chloride in neutral solution; Linke (30) has quoted the solubility as $\sim 8.0 \text{ g L}^{-1}$. This property is attractive because the losses of silver in processing solutions have often ascribed to the insolubility of AgCl. Russian workers (31) have studied the kinetics of AgCl dissolution in thiourea solution and in other complexing agents. They found that thiourea ($\text{pH} = 7$) dissolves AgCl just slightly less quickly than cyanide ($\text{pH} = 10$), but faster than sodium thiocyanate or ammonia. In acidic thiourea solution, the rate of dissolution is 6.5 times slower than in neutral solution; this was attributed to the

slow decomposition of thiourea in acid media. In basic solution, thiourea did not dissolve AgCl at all; thiourea itself is very unstable at pH >7.

In neutral and acidic solutions, silver and thiourea combine to form soluble complexes. Fyfe (32) has reported that thiourea added to a solution of silver nitrate caused a precipitate to form. Precipitation continues until the molar ratio of tu:Ag(I) = 1:1. As more thiourea is added, the silver redissolves, and the maximum solubility occurs at tu:Ag(I) = 3:1. This indicated that the complex $\text{Ag}(\text{tu})_3^+$ was formed; the pK (log β) was reported to be 13.05.

The magnitude of the stability constant indicates that silver and thiourea form a strong complex. For example, if a solution initially containing 0.001 molar of silver nitrate at neutral pH is mixed with 0.050 molar thiourea, the amount of uncomplexed silver after equilibrium is attained would be 7×10^{-13} molar. Virtually all of the initial amount of silver would be tied up as soluble $\text{Ag}(\text{tu})_3^+$.

This same species has been identified in water-alcohol-silver nitrate-thiourea (33), acetone-water-silver nitrate-thiourea (34), and water-silver nitrate-thiourea (at ionic strength 0.8 and pH = 5) solutions (35). Compounds where the tu:Ag ratio is 1:3 have been isolated in the solid state; for example $[\text{Ag}(\text{tu})_3]_2(\text{CrO}_4) \cdot 2\text{H}_2\text{O}$ (36) and $[\text{Ag}(\text{tu})_3]_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (37). In these compounds it has been found that the sulphur atom of the thiourea is coordinated to silver. The $\text{Ag}(\text{tu})_3^+$ complex is fairly stable in solution and can be precipitated only by large anions which favour solid formation through lattice energy effects.

When halides are present in solution, the thiourea compounds formed are somewhat different. In $\text{AgNO}_3\text{-KCl-tu-H}_2\text{O}$ media, solid $\text{Ag}(\text{tu})_2\text{Cl}$ formed (38) and in thiocyanate solution, $\text{Ag}(\text{tu})_2\text{SCN}$ was separated (39).

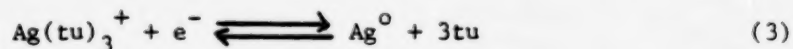
Similar complexes have been postulated to form with iodide and with the pseudohalide, cyanide, although the compositions were variable (38,40). The crystal and molecular structures of $\text{Ag}(\text{tu})_2\text{Cl}$ have been elucidated (41), and it was found that each silver atom is surrounded by a pseudotetrahedral arrangement of two bridging (to other silver atoms) sulphurs, one terminal sulphur and one chlorine atom. The overall polymeric structure accounts for the relative insolubility of the silver-thiourea-halide compounds. It has been noted, however, that thiourea complexes of silver are considerably more soluble than AgCl . Thus, if the thiourea:silver molar ratio is high enough, the silver should stay in solution due to the formation of $\text{Ag}(\text{tu})_3^+$ complexes.

The foregoing discussions considered neutral media reactions; in acidic solutions, different reactions may occur. When acidic solutions of silver nitrate and thiourea are combined, a compound, $\text{Ag}_2(\text{tu})_3(\text{NO}_3)_2(\text{H}_2\text{O})_{2.5}$, is initially formed. This solid dissolves upon the addition of more silver or thiourea (42). This type of 2:3 complex has been prepared from acidic solutions where chromate, CrO_4^{2-} , is the counterion (36). These compounds have been assigned a polymeric structure (42). Again, the increased solubility at higher thiourea concentrations must be due to $\text{Ag}(\text{tu})_3^+$ complex formation. The fact that higher silver concentrations cause dissolution of the 2:3 compounds suggests that complexes with coordination numbers less than 3 may be significant in acid solutions.

Russian workers have studied the solvent extraction of silver thiourea complexes from sulphuric acid solutions (43) into nitrobenzene. They found that $\text{Ag}(\text{tu})^+$ was extracted from acid solutions whereas $\text{Ag}_2(\text{tu})_3^{2+}$ and $\text{Ag}(\text{tu})_2^+$ were extracted from neutral and alkaline solutions. This behaviour is different from that observed with gold where $\text{Ag}(\text{tu})_2^+$ was the only species extracted over the entire pH range.

This section has shown that silver-thiourea complex formation will readily dissolve silver(I) from various insoluble species. The coordination number of thiourea to silver can vary from 1 to 3 depending upon factors such as silver concentration, thiourea concentration, counterions available, and the acidity of the media.

No experimental work on the electrochemistry of silver in thiourea media has appeared in the literature. The stability constant obtained from the potentiometric experiments ($\log \beta = 13.05$) (32) can be used, however, to calculate the decomposition potential of silver in thiourea solution. The Nernst equation ($E = E_{\text{Ag}^+/\text{Ag}}^0 - \frac{RT}{nF} \ln \beta$) predicts a potential of 0.020 volts for the reaction:



Information on the kinetics of the oxidation and reduction, stabilities of the various products and the effect of other conditions would have to be determined experimentally and thus are unavailable.

The predicted reduction potential of the reaction referred to above is 0.020 volts which is very similar to the 0.022 volts for the Ag/AgCl redox couple. Silver metal would be more noble in thiourea than in thio-sulphate (0.01 V), iodide (-0.15 V), cyanide (AgCN_2^- , -0.31) and sulphide (-0.69). Silver is less noble in thiourea than in non-complexing media such as sulphate or perchlorate. Thus, thiourea is a fairly good lixiviant for silver with the solubility of silver-thiourea complexes enhancing its transfer to the solution phase.

A report has appeared in the literature on the use of the $\text{Ag}/\text{Agtu}_2(\text{ClO}_4)$ electrode for the determination of free thiourea in 1 M HClO_4 solutions (44). The electrode was prepared by electrolyzing a $\text{Ag}(\text{CN})_2^-$ solution onto a platinum electrode to give a silver coating. This silver-coated electrode

was immersed in 0.1 M thiourea - 1.0 M HCl media and anodized at 0.25 mA/cm^{-2} for 40 min. The electrode surface was coated with a light brown deposit which was felt to be $\text{Ag}(\text{tu})_2(\text{ClO}_4)$. From the discussion presented so far in this review, it is clear that $\text{Ag}(\text{tu})_2(\text{ClO}_4)$ would not form, but rather a soluble Ag-tu species would be the result. The light brown solid formed at the surface of the electrode is probably Ag_2S and not a thiourea compound. In some preliminary work on the anodic dissolution of silver in thiourea, it has been found that silver thiourea compounds can decompose to Ag_2S under fairly mild conditions (45).

It is interesting to note that compounds very close to thiourea in structure have been used as specific precipitating agents for silver. The "SCNH" grouping of thiourea is very similar to that of rhodanine and related compounds (46,47). The activity of these latter compounds is related to the acidity of the hydrogen attached to the nitrogen in the molecules. Rhodanine is a weak acid ($\text{pK}_a \sim 5.2$) whereas thiourea is not acidic at all as has already been discussed. Thus, thiourea is not effective in the same way.

THIOUREA IN THE EXTRACTIVE METALLURGY OF SILVER

Gold usually appears as the native metal in its ores whereas silver displays a more complex mineralogy. Although native silver is often not predominant, it can be locally abundant and often forms from the oxidation of sulphide minerals. The common silver minerals are the sulphide, the chloride, and various silver sulphosalts. Silver chloride and silver sulphide are compounds which have low solubility products (K_{sp} 's of 2.8×10^{-10} and 5.5×10^{-51} , respectively (48)). Silver can occur in solid solution in other minerals such as galena, tetrahedrite and chalcopyrite and perhaps in

sphalerite and pyrite. Silver is also easily incorporated into jarosite. The silver materials encountered can be concentrates containing fairly high levels of Ag, concentrates of other minerals with medium or low concentrations of Ag, complex ores or residues containing a low or medium level of silver with a multitude of other minerals present.

When a leaching agent is used for silver extraction, it is necessary to know how selective the reaction has to be, whether an oxidative leach is necessary, and whether the reaction products are stable to the ambient conditions. Not much work has been done on the many diverse silver-bearing materials. As was outlined in the last section, many aspects of the fundamental chemistry of silver and thiourea have not yet been studied. Nevertheless, a few studies have attempted to shed some light on the behaviour of silver with thiourea.

Silver chloride is a very insoluble species which dissolves fairly readily in neutral thiourea media, in a manner analogous to the behaviour in alkaline cyanide solutions. In acidic thiourea, the reaction is not as fast, but it is still effective. Most work on thiourea systems has required acidic conditions so this is a factor. There are no quantitative data on the absolute solubility of AgCl in acidic thiourea media as a function of temperature, acidity (pH) or the presence of other chemical entities.

Some Russian workers (49, unfortunately only available as an abstract) have mentioned that Ag_2S and Ag_2SO_4 are much more soluble in NaCN solution. It would be useful to have more detailed quantitative information on these systems.

Chen et al. (25) and Panchenko et al. (49) have looked at the reaction of thiourea on a rotating silver disk with iron(III) as the oxidizing agent.

Panchenko et al. (49) imply that ferric sulphate was the best oxidant tried although no information was given on the other systems. They reported that the reaction is controlled by ferric ion diffusion at rotation speeds less than 250 RPM; the conditions are not given. Chen et al. (25) found that the reaction rate was dependent upon the ferric ion concentration at 125 RPM, 1% thiourea, 0.5% H_2SO_4 , and 0.04%-0.25% Fe(III). These workers reported that silver metal will dissolve 10.8 times faster in 1.0% tu, 0.5% H_2SO_4 and 0.1% Fe(III) than in 0.5% NaCN and 0.05% CaO solution, a conventional cyanide medium.

Chen et al. (25) also reported the results of thiourea leaching their silver-containing copper concentrate. The thiourea solution (0.5% tu, 0.5% H_2SO_4 , 0.1% Fe(III)) gave better extractions and faster dissolution rates of silver than did cyanide (0.5% NaCN, 0.5% CaO). No details on how silver occurs in the concentrate or on the overall silver recovery were given. No analysis of reagent consumption was attempted although Groenewald's (23) work on gold outlined earlier suggests that this is an important variable for economic considerations. Although the Chinese work was conducted at room temperature and low reagent levels which would minimize reagent losses, it would still be necessary to have quantitative data.

This section demonstrates that the studies done to date using thiourea-silver systems have not nearly begun to address the fundamental chemistry questions or the complexities of real silver processing systems. Even in the studies reported, much is left unsaid. For instance, in the leaching of silver in thiourea-sulphuric acid-ferric ion media, no comparisons were drawn to ferric ion-acid alone or to sulphuric acid-thiourea (FSD) media alone. These latter studies are not available in the literature and it would be useful to check such effects to see whether thiourea has any real effect or not.

Even the methods of recovering silver from solution have not been studied. As pointed out for gold extractive metallurgy, the zinc cementation method would not be effective and other methods, presently not studied, would have to be used.

CONCLUSIONS

Thiourea is a novel hydrometallurgical processing option. The organic molecule, thiourea, can act both as a complexing agent and as an oxidant via formamidine disulphide formation. The poor Bronsted basicity of thiourea allows it to complex metal ions effectively in acidic media. Its good Lewis basicity enables thiourea to form strong complexes with gold(+) and silver(+). These complexes make the metals less noble than in non-complexing media and increase their solubility. Potentially, this may aid the recovery of the metal salts.

The main problem associated with the use of thiourea is the decomposition of thiourea under the leaching conditions. High temperatures, high oxidant levels and high thiourea concentrations tend to favour decomposition. Most thiourea leaches are done at low temperatures ($<40^{\circ}\text{C}$) with low oxidant and thiourea concentrations ($<5\%$). No mechanism to rationalize the thiourea decomposition has been advanced. Thiourea's poor Bronsted basicity precludes the inclusion of protons from acid as having a major effect. It is fairly easy to demonstrate that any work which concludes that acid conditions alone are the sole reason for thiourea decomposition oversimplifies the chemistry involved.

Ferric ion, though useful as an oxidizing agent, consumes the free ligand by complexation and by its oxidative action, decomposes the thiourea to sulphur and other products. Further studies on the effect of Fe^{3+} on

thiourea stability would be required to understand more fully the chemistry involved. It is worthy to note that ferric-thiourea complexes have been used as radical sources for polymerization and this may be a decomposition pathway.

Thioureation of gold ores has shown that thioureation is effective, but uneconomical compared to cyanidation. There may be cases, however, where cyanidation is not useful and thiourea is the only choice available.

The use of thiourea for extracting silver from silver-bearing materials has not been as extensively or intensively studied as for extracting gold. The more complex mineralogy encountered and the greater variety of feeds combined with the deficiency of data make it more difficult to ascertain the effectiveness of thioureation for this purpose. The primary conclusion which can be reached is that much more information must be available before a rational decision can be made.

This survey has indicated that the most advantageous conditions for thioureation would be strong acid, moderate thiourea, low oxidant levels and low temperatures ($\sim 20^{\circ}\text{C}$). Also, there is an absence of data on some aspects of silver thiourea interactions such as electrochemistry and complex behaviour in acidic and acidic chloride media. Further work would be needed to comprehend more fully these effects on the deportment of silver in process streams. Fundamental studies on mineral solubilities and oxidizability would have to be carried out along with more applied work on actual feedstocks to complete the picture.

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